Observations, &c. (*continued*).
    San Fernando :—Instituto y Observatorio de Marina.   Anales (Ob-
        servaciones Meteorológicas).   Año 1888.   4to.   *San Fernando*
        1889.   The Observatory.

"On the Steam Calorimeter."   By J. Joly, M.A., B.E.,
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[Plates 6, 7.]

In two papers read before the Royal Society,[*] some three years
ago, I described a " Method of Condensation " in calorimetry.   A
number of experiments in support of the reliability of the new
method are contained in those papers, as well as a description of such
forms of apparatus as I had then been using.   The apparatus,
however, could not be said to be the result of a very prolonged
study of the capabilities of the method, and possessed many defects,
chiefly on the score of convenience in effecting the measurements.
A continued use of the method since that time and its application to
some exacting measurements have led to various alterations in the
apparatus, so that, after many reconstructions, entirely new forms
have been conferred on the instrument.   I purpose to describe two
new forms : a single calorimeter similar in type to the older instru-
ment, but differing in construction ; and a differential calorimeter,
rendering possible measurements which could hardly be effected in
the single type of instrument.

In the interval, too, a wider knowledge of the capabilities of the
method has been acquired.   Its errors have been enquired into.   On
the question of the errors arising from radiation many hundreds of
experiments have been made.   The general results of these will be
found in the following pages.   Again, I have from time to time tabu-
lated such data as are of use in the applications of this calori-
metrical method.   These I ask permission to include, so as to render
this account of the method as complete as it can, within convenient
bounds, be made.   As, however, descriptions of the principles of the
method, and of many experimental tests to which it has been sub-
jected, are accessible both in Professor Bunsen's paper[†] on the

[*] " On the Method of Condensation in Calorimetry " and " On the Specific Heats
of Minerals," ' Roy. Soc. Proc.,' vol. 41, p. 352 *et seq.*

[†] " Über das Dampfcalorimeter," Wiedemann's ' Annalen der Physik und Chemie,'
vol. 31, 1887, p. 1.

" Steam Calorimeter " (as he has designated it) and in my own papers (*loc. cit.*), I will go over this old ground only so far as to be intelligible to those who have not seen those papers.

Theory of the Method.—The theory of the method is, briefly, as follows :—A substance at the temperature, t_1, of the air brought into an atmosphere of saturated steam will, in attaining the temperature, t_2, of the latter, condense a certain weight of steam, w, such that $w\lambda$, where λ is the latent heat of vapour of water, represents a quantity of heat equal to the calorific capacity of the substance between the limits of temperature. Hence, if S be the specific heat of the body, W its weight,

$$w\lambda = \mathrm{WS}\ (t_2^{\circ} - t_1^{\circ}) \dots \dots \dots \dots \dots \quad (1.)$$

From this S is deduced by measuring w, t_2°, t_1°, W, and knowing the value of λ from recorded experiments.

The apparatus required is one permitting the sudden admission of steam around the substance, and subsequently the accurate observation of the weight of water precipitated upon it.

The steam calorimeter is on the lines of a slight metal receptacle, placed beneath a delicate balance, so that a wire depending from one arm of the balance sustains a light wire platform within the receptacle or calorimeter. The platform is provided with a little platinum-foil catchwater beneath it. The substance to be dealt with is placed upon the platform. Steam being admitted into the calorimeter, the substance rapidly rises to its temperature, condensing steam, which adhering as water to its surface, or dropping into the catchwater beneath, is estimated without loss by the balance. In this way the value of w is determined in the equation for the specific heat.

The observation of t_1° is effected by a thermometer left in company with the substance in the calorimeter a sufficient length of time and read just before admitting steam. The temperature of the steam, t_2°, is deduced by inserting a thermometer in the calorimeter when it is filled with steam or by observation of the height of the barometer. In the thermometry it is sufficient in order to secure a high degree of accuracy to read the second place of decimals by estimation, the thermometers having a fairly open scale divided to tenths of degrees. The range obtaining is so considerable that one tenth of a degree is a small fraction of the whole.

On the Values of the Constants required and the Corrections necessary in the Use of the Calorimeter.

The succeeding pages contain a discussion of the constants required in the use of the steam calorimeter and the mode of applying the necessary corrections.

The Latent Heat of Steam.—The value of λ, the latent heat of steam, may be taken for rough experiments as 536·5, its value at 760 mm. pressure. In accurate work its variability with the barometric height is, however, not negligible. Following Professor Bunsen, and in a great measure quoting from his paper, I subjoin a table containing the value of λ and the boiling point of water at different heights of the barometer. The values of λ are calculated on Regnault's formula for the total heat of steam :—

$$Q = 606\text{·}5 - 0\text{·}695t - 0\text{·}00002t^2 - 0\text{·}0000003t^3.$$

Table I.—Pressure, Temperature, and Latent Heat of Steam.

Pressure in mm.	Temp. of steam.	Latent heat.	Pressure in mm.	Temp. of steam.	Latent heat.
726	98 ·72	537 ·4	759	99 ·96	536 ·5
727	98 ·76	537 ·4	760	100 ·00	536 ·5
728	98 ·80	537 ·3	761	100 ·04	536 ·5
729	98 ·84	537 ·3	762	100 ·07	536 ·5
730	98 ·88	537 ·3	763	100 ·11	536 ·4
731	98 ·92	537 ·2	764	100 ·15	536 ·4
732	98 ·95	537 ·2	765	100 ·18	536 ·4
733	98 ·99	537 ·2	766	100 ·22	536 ·4
734	99 ·03	537 ·2	767	100 ·25	536 ·3
735	99 ·07	537 ·1	768	100 ·29	536 ·3
736	99 ·11	537 ·1	769	100 ·33	536 ·3
737	99 ·14	537 ·1	770	100 ·36	536 ·3
738	99 ·18	537 ·1	771	100 ·40	536 ·2
739	99 ·22	537 ·0	772	1C0 ·44	536 ·2
740	99 ·26	537 ·0	773	100 ·47	536 ·2
741	99 ·29	537 ·0	774	100 ·51	536 ·2
742	99 ·33	537 ·0	775	100 ·54	536 ·1
743	99 ·37	536 ·9	776	100 ·58	536 ·1
744	99 ·41	536 ·9	777	100 ·62	536 ·1
745	99 ·44	536 ·9	778	100 ·65	536 ·1
746	99 ·48	536 ·9	779	100 ·69	536 ·0
747	99 ·52	536 ·8	780	100 ·72	536 ·0
748	99 ·56	536 ·8	781	100 ·76	536 ·0
749	99 ·59	536 ·8	782	100 ·80	536 ·0
750	99 ·63	536 ·8	783	100 ·83	535 ·9
751	99 ·67	536 ·7	784	100 ·87	535 ·9
752	99 ·70	536 ·7	785	100 ·90	535 ·9
753	99 ·74	536 ·7	786	100 ·94	535 ·9
754	99 ·78	536 ·7	787	100 ·98	535 ·8
755	99 ·82	536 ·6	788	101 ·01	535 ·8
756	99 ·85	536 ·6	789	101 ·05	535 ·8
757	99 ·89	536 ·6	790	101 ·08	535 ·8
758	99 ·93	536 ·5			

The Density of Steam and Correction for Displacement.—Allowance must further be made for the change of density of the medium surrounding the substance. This will in many cases amount to a

considerable deduction from the increase of weight indicated by the balance. It is to be remembered that the density of steam at 100°C. is about half that of air at 10°C. The effect on the apparent weight of the substance will in fact be observable even if it displace a volume of but one cubic centimetre, and the deduction becomes very necessary when dealing with bulky substances.

The following table contains the density of saturated steam over the range of barometric variation. It is calculated from the formula of Zeuner,*

$$y = \alpha p^{1/n},$$

in which, when p is expressed in atmospheres, a has the value 0·6061, $1/n$ the value 0·9393.

Table II.—Mass of a Cubic Centimetre of Saturated Steam in Grams.

Pressure in mm.	Grams.	Pressure in mm.	Grams.	Pressure in mm.	Grams.
730	·000583	750	·000598	770	·000613
735	·000587	755	·000602	775	·000617
740	·000591	760	·000606	780	·000621
745	·000594	765	·000610	785	·000625

The results obained from this formula and embodied in the table agree well with deductions based on Regnault's experiments on the total heat of steam. The rate of variation with rise of temperature is closely represented by the formula, but it is noteworthy that the values themselves depart somewhat from Fairbairn's and Tate's experimentally found values.† Thus, according to the latter observers, the density at 100° is 0·0006187. Now, although in general a small error in those values is not of great import—an error of as much as 5 per cent. would most generally have an inappreciable effect on the estimation of w—yet cases may arise when a close value is desirable.

In the hopes of deciding between the various values assigned to the density of steam, I made some direct experiments in the calorimeter. These, in fact, became necessary in the course of some early experiments on the specific heat of air at constant volume, when the displacement difference of a spherical copper vessel having a volume of about 164 c.c. had to be considered. Although the experiments are not as concordant as could be desired, their object is, I think, sufficiently attained. I, therefore, add a short account of them here.

* 'Théorie Mécanique de la Chaleur,' p. 286.
† 'Phil. Trans.,' vol. 150, 1860, p. 185 ; vol. 152, 1862, p. 591.

The procedure adopted was the obvious one of measuring directly the effect of the displacement difference, air to steam, on the weight of the copper sphere; condensation of the steam upon it being prevented by raising it to a temperature above that of the steam before the vapour was admitted into the calorimeter. The calorimeter used was spherical, and 14 cm. in diameter. The sphere was first equilibrated when cold as it hung in the calorimeter, the air in the calorimeter being to a great extent dried by leaving in it a vessel of calcium chloride throughout the previous night. In considering, then, the density of the air in which equilibration was effected, the hygrometric state of the air need not be taken into account. At this point the temperature of the air in the calorimeter and the height of the barometer were observed. Steam was now got up in the boiler attached to the calorimeter, the calorimeter opened, the calcium chloride removed, and the process of heating the sphere begun.

This consisted in applying to it a spirit flame as it was slowly swung round on the suspending wire. Of course the first effect of the flame is to precipitate moisture on the cold metal, but as this grows hot the moisture drys off. To avoid as far as possible a change of weight during this process, due to oxidàtion, the precaution had been taken of subjecting the sphere to a prolonged course of similar treatment previously, till further heating over a reasonable interval of time had no appreciable effect on its weight.

When the temperature of the sphere all over is well above that of the steam, shown by touching it here and there with a stirring-rod wet with water, steam is admitted into the calorimeter.

It is observable that if now, immediately the calorimeter is filled with steam, the counterpoise be adjusted till equilibrium obtains, this counterpoise will be excessive. The steam is superheated in the vicinity of the copper sphere, and its density diminished below its true density at the prevailing pressure. In a few moments the apparent weight of the sphere diminishes. The change may be as much as a milligram. The vibrations of the balance now become steady, and this state of equilibrium continues for from 10 to 14 minutes. The quantity by which the counterpoise has been increased to maintain this equilibrium is the true result of the experiment. Subsequently a slow and uniform increase in the apparent weight of the sphere takes place, at the rate of 1 milligram in five minutes. This effect, which is considered further on, is apparently due to radiation, and consequent slow continued precipitation of water in the sphere. It does not apparently interfere with the experiment. When the experiment is concluded, I found it necessary sometimes to make a second observation of the height of the barometer.

To reduce the experiment the following values are required :—

The volume, V_1, of the sphere at the temperature, t_1, of the air.

„ „ V_2, „ „ t_2 „ steam.

„ reading, p, of the barometer at the time of equilibrating the sphere in air.

„ „ P, of the barometer at the time of equilibrating the sphere in steam.

„ weight, ϖ, added to the counterpoise during experiment.

From these measurements, if D be the deduced density of dry air at the temperature t_1 and pressure p, then the density, δ, of steam (weight of 1 c.c.) at the pressure P, is got by—

$$\delta = \frac{V_1 D - \varpi}{V_2}.$$

This is a close approximation; for if w_1, v_1 represent the weight *in vacuo* and the volume of the counterpoise respectively, when the sphere is equilibrated in air; w_2, v_2, the weight and volume of the counterpoise when the sphere is in steam; and if d be the density of the air prevailing during this last period, and W = the weight of the sphere *in vacuo* ; then first :—

$$w_1 - v_1 D = W - V_1 D,$$

secondly, $\qquad w_2 - v_2 d = W - V_2 \delta.$

Assuming $v_1 D = v_2 d$, as the difference between D and d will be small or non-existent, and $v_2 - v_1$ is also small, and subtracting, δ is obtained as above.

The details of eight experiments effected in this way are contained in Table III. It is only necessary to observe regarding the data of these experiments that V_1 and V_2 were based on a measurement of the volume of the sphere made by weighing it in air and in distilled water in the usual way. After all corrections, the volume was found to be 164·60 c.c. at the temperature 10·50. The volume at the temperatures prevailing during the subsequent experiments was in each case obtained from the formula of Matthiessen,[*]

$$V_{T_2} = V_{T_1} (1 + a (T_2 - T_1) + b (T_2 - T_1)^2),$$

where $a = 4\cdot443 \times 10^{-5}$, $b = 5\cdot55 \times 10^{-8}$.

[*] 'Roy. Soc. Proc.,' vol. 15, 1866, p. 220.

Mr. J. Joly.

Table III.—Experiments on the Density of Saturated Steam at Atmospheric Pressures.

	t_1.	V_1.	t_2.	V_2.	p.	D.	ϖ.	P.	δ.
						0·00			0·000
1	19·12	164·67	99·96	165·33	758·90	12066	0·098	758·90	6090
2	10·20	164·60	100·31	,,	768·56	12604	0·1065	768·56	6092
3	10·55	164·60	100·37	,,	770·18	12617	0·1065	770·18	6106
4	8·68	164·58	100·28	,,	768·30	12668	0·1075	767·76	6094
5	8·49	164·58	100·19	,,	765·25	12626	0·1070	765·25	6097
6	7·54	164·57	100·17	,,	765·30	12672	0·1080	764·85	6081
7	8·59	164·58	100·13	,,	763·68	12596	0·1065	763·68	6097
8	8·79	164·58	100·05	,,	761·49	12551	0·10625	761·49	6067
Mean values......			100·18	..	..	..	..	765·08	6090

On comparing the result deduced as the mean of these eight observations with the value tabulated opposite the pressure of 765 mm. in Table II, it is seen that the experimental value is practically identical with that derived from Zeuner's formula. From the experiments 0·000609, from the formula 0·000610. I have thought, then, Zeuner's results probably the safest to adhere to of the many estimations that have been advanced for the density of steam at atmospheric pressures.

The method of using Table II is obvious. The volume of the substance estimated in cubic centimetres is multiplied by the suitable value taken from the table. This is the displacement in steam. The displacement in air must also be estimated for the prevailing temperature, t_1, and pressure, by reference to a table of air densities, as the difference of the two is, of course, that which affects the observation of the weight of the substance transferred to an atmosphere of steam.

If it be desired to secure the observations from error as far as possible at all points, then two further corrections on the value of w are necessary :—(1.) An allowance for the change of volume of the substance due to thermal expansion in passing from air temperature to steam temperature. This may be considerable in the case of metal vessels or large masses of metal. This correction is additive to the value of w. (2.) A correction for the displacement in steam of the precipitated water, *i.e.*, the reduction to *vacuo* of the weight of water w. This is also an additive correction.

Both these corrections are included in the following equation for the true weight of condensation, w,

$$w = \frac{w_1 - V_1 D + V_2 \delta}{1 + \delta}, \quad \dots\dots\dots\dots\dots\dots \quad (2.)$$

where V_1 = volume of the substance at t_1,
$V_2 = $ „   „ t_2,
$D = $ density of air at t_1 and prevailing pressure,
$\delta = $ „   steam at prevailing pressure,
$w_1 = $ the weight added during experiment.

This formula departs from strict accuracy only in so far as it assumes unit mass of water to occupy unit volume at the temperature of the steam.

Approximate Correction for Displacement.—In a great many cases, the vast majority of cases, indeed, it will be sufficient to substitute for the foregoing a far simpler correction based on the density of steam relative to air. Assuming a mean pressure of 760 mm. :—

For air at   0° the relative density is 0·00069,
    „   5°   „   „   0·00066,
    „   10°   „   „   0·00064,
    ·,   15°   „   „   0·00062,
    „   20°   „   „   0·00060.

The volume of the substance in cubic centimetres is to be multiplied by the most suitable of these factors to ascertain the amount to be deducted from the apparent weight of condensation.

Correction for the Carrier.—A deduction, from the observed weight of precipitation, due to the calorific capacity of the carrier is of course necessary. This is effected on a previous experiment (or experiments) on the empty carrier and proportionately to the relative extent of the ranges in the two cases.

On the Accuracy of the Method and the Error arising from Radiation.

Many experiments bearing on the accuracy of the method are contained in my former papers. It is sufficient to say here that :—(1.) Successive experiments on the same piece of matter, whether a good conductor of heat or a bad conductor, show one with another a consistency of result exceeding that found in the records of observations by other methods, as in Regnault's experiments, using the method of mixtures on a very elaborate scale, and dealing with very large quantities of matter. (2.) The results obtained, both with good conductors and bad conductors, agree closely with the most reliable determinations of Regnault, Bède, Mallet, &c. (3.) Wide variations in extent of surface, and in the quantity of the substance placed in the calorimeter, fail to affect the consistency of the result. I will explain with one example. A limpid crystal of barytes weighing 76·109 grams, placed in the calorimeter, afforded 0·10923 as the mean specific heat between 9·65° and 100·30°. It was now broken up into small fragments, which were piled up on the carrier : 65·143 grams were thus returned to the calorimeter. These afforded 0·10910 as the mean specific heat over the range 9·60° to 99·80°.

This no mere accidental coincidence.* It is certainly exceptional for repetition experiments to differ by more than half per cent. With ordinary care, indeed, they are quite as faithful and as sure as repetition determinations of specific gravity made in the ordinary way, and on similar quantities of matter.

It is to be added that since the experimental evidence in support of the method was published much has been done, using various modifications of the apparatus. I have found that the results in

* A table containing many such experiments is contained in my paper " On the Method of Condensation," p. 362.

every case were consistent from one apparatus to another. In large or small calorimeters, with varying dimensions of steam-pipe, boiler, or exit tube, the consistency of result was maintained. Thus the single calorimeter described further on will be found very different in the disposition of its parts from the form designed for use within the case of a balance as described in my former paper. In the course of some recent experiments on the mineral sulphides, I desired to check in some cases former results, by dealing over again with the specimens dealt with in the first calorimeter. I have collected these cases here.

	W.	$t_1.$	$t_2.$	$w.$	sp. h.
Galenite, cleavable fragments—					
Former result	56·967	10·50	99·90	0·496	0·05224
Another former experiment ...	56·951	10·98	99·76	0·493	0·05232
,, ,, ,, ...	56·951	11·77	99·70	0·487	0·05219
Experiment in new calorimeter	56·759	18·05	100·00	0·4545	0·05242
Another specimen, close-grained—					
Former result	87·840	13·27	99·60	0·6955	0·04921
Result in new calorimeter	93·817	17·65	100·10	0·7141	0·04952
Sphalerite, cleavable, high lustre—					
Former result	45·765	11·80	100·18	0·863	0·11445
Result in new calorimeter.....	45·755	16·25	99·80	0·8151	0·11442
Pyrite, two interpenetrated cubes—					
Old result	46·710	10·50	99·90	1·016	0·13111
Recent result..............	46·710	17·50	100·00	0·9375	0·13052

As regards what is probably occurring in the calorimeter, it is convenient to consider the duration of an experiment as divided into a period in which the substance is rising in temperature, and a period in which, having attained the temperature of the steam, it hangs surrounded by an atmosphere of saturated vapour, while its weight is being determined. I briefly epitomise, in part from my former paper, the following considerations. Throughout the first period :— (*a.*) The film of water, which is almost immediately formed upon the substance, is having its outer surface continually renewed by precipitation of fresh steam, and hence presents a surface but slightly cooler than the surrounding steam. (*b.*) This film of water will be very adiathermanous to radiation from water vapour, so that most of the steam will condense, not by radiation, but by contact with the slightly cooler outer service of the water-layer. (*c.*) A reduced pressure will obtain, or tend to obtain, around the substance, giving

rise to an inflow of the surrounding steam. This condition tends to correct what error might arise from radiation from points in the vapour near the surface of the body. Vapour so precipitated will, in fact, be carried by the indraught and thrown upon the substance. In view of this, care is taken so to construct the calorimeter that no sharp cross-draughts play upon the substance on the entry of the steam, which might possibly diminish the protective effect of the indraught. (d.) It is possible that during this first period, if the walls of the calorimeter heat more quickly than the substance, some radiation might occur from the walls to the substance, appearing as a minus error in the result. It is to be added, however, with regard to (d) that the entire duration of this first period is very short, and that the quantitative results of experiments on substances show complete independence of surface conditions.

During the second period, in which the weighing is effected, the substance is to be considered as surrounded by a medium which, without change of temperature, maintains the inner surface of the walls of the calorimeter uniformly at the temperature of the substance or very nearly so, and which itself acts as a screen very opaque to radiation. So that, so soon as the substance has ceased absorbing energy, the conditions are very favourable to preserve it from the effects of further action from radiation. Nevertheless, there is an amount of radiation effect continuing uniformly during this period, and this on a sensitive balance is perceived by continued observation. This was first pointed out to me by Professor Himstedt, of Darmstadt, who, after the appearance of the papers on this method of calorimetry, kindly sent me the results of his observations on instruments of the types described both by Professor Bunsen and by me. He found the weight of the substance hanging in the steam was not absolutely constant, but was subject to an accretion of some 3 or 4 milligrams in an hour.

As it was desirable to ascertain the cause of this increment and how far it could be reduced, and as, too, it was quite conceivable that occasion might arise when allowance for it would have to be considered, I made a considerable number of protracted observations upon it. It is sufficient to observe here that the effect seems with most probability a radiation effect. It is greater for rough than smooth bodies. Lamp-blacking the substance, or the inside of the calorimeter much increases it. Cooling the outside of the calorimeter, as by spraying cold water upon it, increases it. Calorimeters with double walls, having bright reflecting surfaces, show less increment. For large calorimeters it is less than for small ones. It is uniform or nearly so for however long the experiment is continued. On the other hand, increase of the rate of flow of the steam through the calorimeter does not seem to affect it, which appears to differentiate it from any-

thing like an effect due to mechanically suspended water in the steam. It appears, in fact, to arise from a slow loss of heat from the substance to the walls of the calorimeter, steam, in consequence, condensing on the substance.

The numerical results of my own experiments, effected in a large, single-walled calorimeter of spherical form, 14 cm. in diameter, are such as to afford :—

> 3 milligrams per hour on a clean, blown glass sphere having a surface of 80 sq. cm.
> 4 milligrams per hour on a dull surface of platinum of 80 sq. cm.
> 8 milligrams per hour on a lamp-black coated surface of 80 sq. cm.

These results were obtained using a roomy calorimeter.

From experiments in a calorimeter of the type to be presently described, but somewhat smaller (8 cm. in diameter) and double-walled only on the lower, removable part, I take the following :—

(1.) A clean, but not bright, copper box, cylindrical in form, having an external surface exposed to the steam of 52 sq. cm. nearly, standing in a platinum-foil catchwater, exposing an effective surface of 57 sq. cm. ; total 109 sq. cm. of clean metal, showed an increment of from 0·45 to 0·5 milligram per 5 minutes. Thus successive observations of the increment every 5 minutes afforded :—

$$0·4 \quad 0·5 \quad 0·4 \quad 0·4 \quad 0·4 \quad 0·5 \quad 0·5 \quad 0·5.$$

The inside of the calorimeter in this experiment was smooth and clean. Later I made the experiment of gilding and burnishing the inside surface of the calorimeter. This appeared, however, to make no sensible difference : thus, with all otherwise as above, observations gave the increment per 5 minutes :—

$$0·5 \quad 0·5 \quad 0·5 \quad 0·5 \quad 0·5 \quad 0·5.$$

(2.) A rough block of cryolite weighing 37 grams, resting on the platinum catchwater as above, gave 0·74 milligram per 5 minutes ; the observations were :—

$$0·7 \quad 0·8 \quad 0·7 \quad 0·8 \quad 0·7.$$

(3.) The catchwater of platinum foil alone, with stirrup, as described in (1), in the calorimeter previous to gilding its interior gave the increment, determined every 5 minutes :—

$$0·2 \quad 0·3 \quad 0·3 \quad 0·4 \quad 0·3 \quad 0·4 \quad 0·5 \quad 0·3$$
$$0·3 \quad 0·4.$$

Mean increment, 0·34 per 5 minutes.

(4.) The stirrup, which is of silver tarnished to blackness, and the cross wires serving as the platform, without the catchwater, gave :—

<div align="center">

0·1   0·1   0·2   0·1   0·2

Mean, 0·14 per 5 minutes.

</div>

I have chosen these observations out of a large number of various experiments as sufficient to give a good idea of how far this radiation effect should be considered in observations made with this calorimeter. But before dealing further with this question a few more experiments must be added.

(5.) Frequent observations with sensitive thermometers failed, even under extreme conditions, to reveal radiation across the steam to the walls of the calorimeter. These experiments were conducted in this manner. A very delicate thermometer, removed from a hypsometer, was coated thickly with lamp-black over the bulb, which measured some 4 cm. in diameter. This was arranged so that the bulb occupied the centre of a spherical brass calorimeter, single walled, and left clean on the inside. Diameter, 14 cm. Steam was admitted and the position of the mercury in the projecting stem of the thermometer observed through a telescope. Cold water was now plentifully sprayed over the surface of the calorimeter, but, although an observer attentively watched the thermometer through the telescope while this was being done, no change in the position of the thread of mercury could be detected. All this time the abundance of evaporated water rising from the outside of the calorimeter and the increased drip from the inside showed that heat was rapidly passing through the walls. This experiment is surprising, perhaps, but if the extreme smallness of the effect indicated in the weight-experiments be considered, it need not, I think, negative the suggestion that the increment is a radiation effect.

(6.) It remains to add what is perhaps the most conclusive experiment on this radiation question—the experiment of coating the inner walls of the calorimeter with lamp-black and comparing the rate of increment with the rate obtaining in the absence of this coating. The increase of surface with the lamp-black is the greater, as the many tiny globules of water condensing from the steam and adhering to the inner wall become each coated with the rough black deposit. Steam was first passed through the space between the walls of the calorimeter till all was heated. Had this not been done, the deposit of lamp-black would have been washed away from the inner surface by the copious condensation. When the steam had been some 5 or 6 minutes in the calorimeter, the current through the jacket was stopped and observations begun. It is to be observed that the presence of moisture between the walls would tend to diminish the protective

effect of the jacket, increasing radiation. With everything else as in
(1) [*ante*], observations every 5 minutes gave :—

<div align="center">

3·4   4·0   3·6   3·0   3·8   3·2.

Mean, 3·5 milligrams per 5 minutes.

</div>

(7.) The lamp-black was now removed and the inside cleaned.
With the same order of procedure as before exactly, and everything
the same except for the absence of the lamp-black, the results
are :—

<div align="center">

0·7   0·7   0·8   1·1   1·1   0·8   1·0,

or nearly 0·9 milligram per 5 minutes.

</div>

The effect of the water deposited between the walls of the jacket is
probably seen in the difference between this experiment and the results
of (1). The difference existing between the results of (6) and (7) is
conspicuous and so far as I can see can only be explained in the hypo-
thesis that the increase is due to radiation. The inference is strong
that the ordinary effect is also in some degree, if not entirely, of the
same nature.

When in special cases it is thought necessary to allow for this effect
of radiation (as I will call it), I would suggest making an observation
on the amount of the increment, say over 10 minutes, subsequent to
the weighing being completed, and deducting proportionately to the
time occupied in weighing—not proportionately to the time since the
first admission of steam into the calorimeter, as I do not think it is
warranted to assume that the same effect obtains during the period in
which the substance is rising in temperature. It is to be remembered,
in fact, that (as before observed) an effect of the opposite sign as
affecting the observed condensation on the body may then have
obtained. It is to be observed that some of the increment will be
due to the carrier. This would have amounted to rather more than
one half in such a case as (2), considerably more in (1). The ordinary
deduction from the total condensation for the calorific capacity of
the carrier will eliminate approximately this portion of the radiation
increment.

But it may be asked: how is it to be determined at what precise
moment the true precipitation has ceased ? when has the substance
attained the temperature of the steam ?

In considering this question it is necessary to realise the nature of
the phenomena observed in the course of an experiment. Suppose
the 37 grams of cryolite, previously referred to, was being dealt with.
Steam is admitted. For three minutes, about, we try in vain to
equilibrate the balance. Equilibrium is impossible for the reason
that condensation is progressing so rapidly upon the cryolite that so
soon as an approximation to equilibrium is obtained this is again

immediately disturbed. The gain is so rapid during this period that weighing, or observation of the rate of increase, is impossible with the ordinary balance. Between this state of things and that prevailing subsequently, when weighing has become possible, there is, of course, no abrupt transition. But, as observed, it is found simply that weighing (in such a case as I am considering) has become possible, probably in the course of the fourth minute. Let the vibrations of the balance be now observed. The oscillations are perfectly regular for about one minute. If the balance reads tenths of milligrams, a slight preponderance of weight will probably be then observable. Watching the vibrations for 5 minutes from the fourth minute, suppose, and then moving the rider till there is equilibrium, the gain is found to be seven-tenths of a milligram. Observing the balance for another period of 5 minutes, the result is again seven-tenths, and so on. However long observation is carried on, the gain is seven or eight-tenths per 5 minutes.

Now this is certainly not due to heating of the substance, and it is established by the observations that the seven-tenths of a milligram represents an uniform rate of increment. But from the fourth to the ninth minute observation gave but seven-tenths. It is safe, therefore, to conclude that by the end of the fourth minute the true condensation due to the calorific capacity of the substance has ceased.

It remains to consider numerically the importance of this source of error in affecting the degree of accuracy attained by this method of calorimetry. I will illustrate this effect by assuming an extreme case in which the increment is entirely ignored, no correction being made for it except the unconscious one made in effecting the deduction for the carrier, and I will suppose that after weighing has become practicable 10 minutes be allowed to elapse, in order to put the temperature of the substance beyond question. I will consider, both in the case of a non-conductor of heat and in the case of a good conductor, the consequent effect on the accuracy of the result.

(*a.*) For the former I cannot do better than take the case of the piece of cryolite referred to in (2). It weighs 37 grams. For a range of 90 degrees I get from an experiment on this specimen ("Specific Heats of Minerals," p. 263) that there would be a condensation of 1·588 grams due to the calorific capacity of the cryolite alone. The increment during the time of observation, according to (2) [*ante*], will be $0·74 \times 2 = 1·48$ milligrams. Observations on the carrier over a similar interval have, suppose, been made once for all. The deduction due to its thermal capacity then reduces the radiation effect by $0·34 \times 2$ or $0·68$ milligram; leaving a + error of 0·8 milligram. This is an error of 0·05 per cent., or 1 in 2000, on the specific heat determined.

(*b.*) Let the case be that of a piece of copper having the dimensions

of the copper box referred to in (1), that is, a cylinder 3·65 cm. in diameter × 4·50 cm. in length. This will be about 405 grams of copper, giving through a range of 90° a precipitation of 6·343 grams of steam. The increment in 10 minutes, less that of the carrier, is $0.5 × 2 - 0.34 × 2 = 0.32$ milligram. The error introduced by neglecting this is 1 part in 20,000 about.

These figures afford an idea of the extent to which this radiation effect, if neglected entirely, affects the results obtained in these calorimeters. And, in practice, even these are excessive ; they double the error actually obtaining, for it will be found that half the interval assumed for observation will be more than sufficient in order to be quite sure of the weighing, and of the condition of the substance when of such dimensions as I have assumed.

What radiation error then can be detected with this method of condensation is not alone in general extraordinarily small, but its amount is easily ascertained, and a close approximation to its entire elimination possible. To the question whether undetected error from radiation or other causes enters into the quantity of steam precipitated upon the substance in the first instance an answer, based on direct experiment, cannot be given. Comparative experiments on substances, using other methods, would not afford a conclusive answer, as the exact extent of the error entering into other methods is at least equally open to surmise. It is to be said, however, that, *a priori*, no grave error is to be expected, and what experimental tests have been applied appear to show that such error if existent must be very small. I have mentioned the general results of these tests.

The Construction of the Steam Calorimeter.

What is the best form to confer upon a steam calorimeter ? There are so many conditions to fulfil that the choice is really not very large. It must permit of being filled rapidly with steam, which should preferably descend in the calorimeter, as it then mixes less with the air. Arrangements must be made for allowing a slow current or circulation of steam to continue all the time the weighing is being effected. This must be such as will not interfere with the accurate determination of the weight. If this circulation of steam be stopped at any time there is a minute but definite fall in temperature. A sensitive thermometer will show this. It is about the one-thirtieth of a degree. If the current be stopped when the body is accurately poised, and after an interval be started again, a minute increase of weight is at once apparent. The substance has cooled in the interval and is reheated on re-establishing the current.

Although this current of steam may be quite slow while weighing is proceeding, there must be complete control over it, so that it may

be made rapid at first when air and mist are being swept out, as the object then is to let in the pure steam as quickly as possible around the substance.

The construction at the point where the suspending wire passes through to top of the calorimeter, ascending to the balance, must be such that no rubbing of the wire in its vibration up and down occurs. That is, the wire should hang in the centre of the necessarily small orifice provided for it; as this is a troublesome adjustment, an automatic arrangement should be provided. No condensation of steam must occur on the wire where it passes out, or above that point, and steam must be hindered from passing up along the wire into the balance.

To effect the accurate determination of $t°$, it is important that the temperature in the interior of the calorimeter change slowly. This necessitates that the walls of the calorimeter be fairly non-conducting. They must withal be light, or they will remain hot an inconveniently long while after an experiment, and will take long to heat, which hinders the rapid filling of the calorimeter with steam.

The interior of the calorimeter must be easily got at for drying out and cleaning, and for putting the carrier readily in its place. It should fit together fairly steam tight, and be simple in construction, and so cheaply made.

A sectional elevation to a scale of one-fourth of a convenient form of the calorimeter is given in Pl. 6, fig. 1; I have worked a good deal with it, and have found it fulfils the requisite conditions.

I may observe that, as regards the condition of preserving a steady internal temperature, no form not very cumbersome will confer perfect satisfaction if used in a room in which a rapid variation of temperature is suffered to occur just before an experiment. In every case it will be necessary to carefully screen off the boiler supplying the steam, so that the waste steam and hot gases from the burner pass up a flue or directly out of the room. It would be best of all to locate the boiler in a neighbouring room, taking a steam pipe through the wall. I have myself suffered more from defect in this part of the arrangements than any other, and what discrepancies occur from one experiment to another I attribute to unsteadiness of the initial temperature. I generally find that in the fifteen or twenty minutes during which the boiler is heating, the thermometer in the calorimeter may show a variation amounting to one-tenth, often to one-fifth, of a degree. My practice is to take three readings during that interval, one just before lighting the burner beneath the boiler, a second when steam is up, and a third just before making an experiment, after the steam has been let flow freely out of the boiler up a flue for eight or ten minutes to clear air and mist out of the boiler. I assume the mean of these three as the

mean temperature of the body if a bad conductor. I take the last if a good conductor. In any case the error introduced will be small, but, of course, it is to be avoided.

It is seen in section that the calorimeter is double walled. The carrier and catchwater are shown hanging within it. In form it is cylindrical, the inner cylinder being cone-shaped at each end. The pitch of the upper cone is made so high that drops of water will run down it, and not fall off it. It is of brass, very thin, the inside being gilt and burnished. This is not essential, but keeps it very clean from the sulphur and antimony which are carried from the rubber steam-pipe by the steam. The surfaces between the walls are simply burnished. Outside it is covered with well-shrunken cloth. The steam admission way is in the upper part of the calorimeter, and by this pipe this upper part is securely fixed to the upright supporting the table carrying the balance. The lower part is entirely removable from the upper. It meets it on a well-ground surface, and is secured in its place by an external bayonet catch at either side. Steam is admitted by the brass pipe shown in position at the other side of the upright. This pipe is removable and is very readily laid in its place, being guided by a hollowed-out wooden support attached to the base board of the calorimeter-stand. It is connected by a thick rubber tube, 2·4 cm. in internal diameter, with the boiler. This tube must have a fall the whole way to the boiler to keep it from choking with water. On steam being admitted, it rapidly drives out the air, the steam descending in the calorimeter. To allow the air to escape, a means is provided for opening the lower orifice of the calorimeter fully. This is effected by rotating a milled-headed screw projecting at the side of the stand, and shown dotted in the section. The shaft from this screw passes across the face of the upright board carrying the calorimeter, and is furnished with two projecting arms. One of these is provided at its extremity with a hard-wood cup, shown dotted, in the depressed position. The other carries a conical catchwater of brass with a sloped brass tube attached, shown in position at the lower orifice of the calorimeter. Either of these, the wooden cup, or the cone and tube, may be brought to cover the orifice in the calorimeter by a longitudinal movement (of about 2·5 cm.) of the shaft of the milled-headed screw. Before experiment the non-conducting wooden cup closes the orifice. Just before coupling with the boiler, this is depressed and pushed back. When it is judged from the appearance of the steam escaping at the orifice that all air is expelled, the cone and tube are elevated against the orifice, closing it except for a slow current of steam still free to issue from the sloped tube. The water draining from the calorimeter also issues through this tube, falling into a dish placed to receive it.

The thermometer for reading the initial temperature is inserted in

the fixed upper part of the calorimeter. It is at a convenient slope
for reading, and its bulb penetrates into the calorimeter till just over
the substance placed on the carrier. In careful work it is well to
read the thermometer by a telescope. A very accurate, but less con-
venient, way is to read with a lens, which is moved about till the
image of the last graduation on the stem of the thermometer reflected
in the thread of mercury is seen to be covered by the graduation.
There is then no parallax error. The thermometer is withdrawn just
before letting in steam, and the tubulure plugged with a small cork.
After the weighing is finished, a thermometer for reading the boiling
point may be inserted in this tubulure. Previous to the admission of
steam, the tubulure taking the steam-pipe is kept closed by the
stopper of wood overlaid with cloth, shown dotted in its position.
The side pieces which go towards supporting the table for the balance
are cut out as shown at each side, so that the operator can see to
remove the stopper, and insert the steam-pipe rapidly. My practice
is to pinch the rubber tube conveying the steam for the moment in
which the steam-pipe is being laid on; when in position it is released,
and steam let flow into the calorimeter. The steam-pipe is in part
covered with thick baize, so that it may while hot be grasped by the
hand.

A section, fig. 2, Pl. 6, full size, shows the arrangement adopted to
render the wire in its passage through the roof of the calorimeter
self-adjusting in the centre of the orifice provided for it, or rather to
render the orifice self-adjusting on the wire. The coned roof of the
inner wall of the calorimeter is carried through the external cylindrical
jacket, flanged at the top, and ground smooth. A loose coned piece
also with ground flange rests on this. The upper end of this cone is
turned down to a knife edge, and just brought flat on a fine stone.
On this a tiny disk of copper or brass drilled centrally with an orifice
about two-thirds of a millimetre in diameter is laid looosely. The
wire bearing the carrier is brought through this disk, which weighs
about 22 milligrams. Above the disk is placed a spiral of fine
platinum wire held in a forceps, which by two binding screws may be
put in circuit with a battery. Through this the wire also passes.
Finally, before the wire rises into the balance, it is embraced by an
inverted cone (fig. 1), turned in hard wood, which is adjustable in
position, being held to the under face of the table by two spring
clips, as a slip is held on the stage of a microscope. On the table a
balance, not shown in the figure, stands. The wire ascends to the
left arm of this balance.

The adjustment of the suspending wire is very obvious. The
balance is set so that the wire hangs freely through a large aperture
in the table provided for it. The inverted cone and the small cone
on the calorimeter are next set to let the wire pass centrally. The

aperture in the inverted cone is about 2 mm. in diameter, that in the lower cone about 3 mm. Their adjustment, therefore, does not present any difficulty, and once made need seldom be disturbed. The disk resting on the lower cone is permitted to adjust itself. During an experiment, it is kept warm by radiation from the platinum spiral, which is put in circuit with a storage cell. It thus remains dry and quite free to move about on the knife edge of the cone. As the wire swings about, it carries it with it from side to side. Finally, when the amplitude of the vibrations diminish sufficiently, it leaves it correctly adjusted, for, of course, the swinging wire will always so shift the disk as to swing in a diameter of the orifice. This arrangement I have found to act very perfectly. The adjustment of the wire in the old arrangement was very troublesome; it demands no attention with this, which in no way interferes with the weighing. The disk should not be lighter than the weight specified, for if too light the amount of steam pressure which it is necessary to maintain will raise it at one side.

It is remarkable as regards the platinum spiral for maintaining the orifice dry that an error may be introduced if this is kept at too high a temperature. It apparently then sets up an ebullition of the water precipitated on the upper part of the calorimeter, the result being a splashing or rain upon the substance hanging below. I have been led to suppose this by observing that the radiation effect is apparently increased by heating the spiral excessively. On the other hand, too cold a spiral, of course, also causes error by permitting water to condense on the wire both above and below the orifice. The right temperature seems to be that which gives to the spiral a just visible red when steam is *not* in the calorimeter. The effect of the up draught of steam is to cool it.

The suspending wire should be of platinum; about 0·1 mm. diameter will be sufficiently strong for most purposes. This ascends to the left end of the balance beam, being directly attached to a counterpoise equilibrating the right-hand pan.

It is well to load the balance till there is equilibrium when the empty carrier is in position. The counterpoising of the substance before an experiment then affords its weight, with, of course, the ordinary correction for air displacement, if thought necessary.

The balance used by me is a Sartorius short-beam (14 cms.). The cheap form of this instrument answers admirably, reading accurately to tenths of milligrams when loaded with over 100 grams. It will do so, I believe, up to 200 grams. It is quick, and in every way is perfect for the purpose. On removing the pan stops the suspending wire may be taken through the drilled aperture left in the plate-glass base.

The stand of the calorimeter is of well-seasoned mahogany, strongly

fitted together. To enable it to be levelled, it is supported on two levelling screws in front and a centrally placed foot at the back. To afford more vertical room, the base board is cut out centrally in front. The carrier for supporting the substance within the calorimeter is shown in position within the calorimeter. It is made of silver wire, about 0·5 mm. in diameter. The catchwater is of thin platinum-foil, and is removable for drying and cleaning. It is, in fact, supported on a projecting claw beneath the ring of the carrier. Across this ring fine platinum wire is stretched, forming a platform on which the substance may be laid. Four wires crossing at the centre will in general be sufficient. When resting on these the substance is exposed to the steam on all sides. The total weight of the carrier is just 3 grams. It condenses about 0·031 gram through a range of 90° C.

The claw supporting the catchwater performs a double function. In the case of a smooth body, which is also a good conductor of heat and of large thermal capacity, such as a thin vessel filled with water, the precipitation is so copious and sudden that it reaches the catch-water before it attains steam temperature. The result is a secondary precipitation on the outside of the catchwater. This might be in some cases so plentiful as to drop from the bottom of the catchwater, and so be lost. The claw serves to entangle this, retaining it on the balance.

It is important that an ample supply of steam should flow into the calorimeter on connecting it to the boiler. To make certain of this, a strong gas-burner and a large boiler should be used. The supply, indeed, should be considerably in excess of what passes up the connecting-tube. If this is not so there is risk of air entering the boiler on first coupling it with the calorimeter, which, mixing with the steam, causes a mist of the cooled vapour to flow up the tube. The danger of this is considerable, as there is a strong tendency to an indraught at the boiler, owing to the buoyancy of the water-gas in the ascending tube. In some experiments on the value of the radiation effect, before alluded to, this came strikingly to my notice. The boiler was fitted with a pressure-relief arrangement, consisting simply of a tube taken externally from the top of the boiler, bent twice at right angles and brought downwards, so that it opened at a level below the bottom of the boiler. Thus a certain small pressure of steam in this was necessary to drive the buoyant gas down this escape-pipe.

Hence I concluded that the continued appearance of steam escaping at the relief-pipe was a sufficient indication of an excess of internal pressure. However, in my experiments a large and unaccount-able increment to the weight of precipitation on the substance pre-vailed, and this I traced after much trouble to the entry of air at the relief-pipe. There was, in fact, a circulation of air and steam within

the tube and boiler ; air entering and flowing along one side of the pipe, steam issuing along the other. On narrowing the opening of the tube, so that a well-defined current of steam having the full section of the tube issued, the effect disappeared. The foregoing method of providing for the exit of the surplus steam is defective and unsafe. It is preferable to use a non-return valve of some sort. I find the simple arrangement shown on the boiler in Pl. 7 (scale one-tenth) very effective. It is simply a balanced flap-valve, meeting the vertical exit-tubulure on a ground edge brought fine, so as not to stick with precipitated water. The counterpoise to the weight of the flap can be placed at discretion in one of several notches near the end of the beam, so that the pressure may be increased or diminished. To keep this valve from falling into vibration, the pivot on which it turns bears at one end against a screw, which may be tightened so as to retard a little the oscillatory motion of the beam. The pressure maintained should be small, as pressures appreciably in excess of atmospheric pressure interfere with the working of the calorimeter. The valve should therefore be so set that it just falls shut readily when steam is not issuing. This, according to measurement, in the case of the valve used by me corresponds to rather less than a pressure of 1 mm. of water. The material of the boiler is copper, tinned within. The burner is a large "solid flame" of Fletcher.

Method of Carrying out an Experiment.—I will suppose the calorimeter dry and cold, and ready for the introduction of the substance. This is placed on the carrier which hangs within the calorimeter dependent from the balance. Having adjusted the substance centrally on the carrier, and so that there is no fear of water dropping from any protruding point of the substance over the edge of the catchwater, and so escaping estimation by the balance, the thermometer for taking the initial temperature of the substance is to be inserted in its tubulure. This is done now, before closing the calorimeter, in order to see that its bulb does not strike against the substance or the stirrup of the carrier, and that it is inserted sufficiently far to be well over and close to the substance. The substance should now be roughly counterpoised by placing weights in the right-hand pan of the balance, and before the final adjustment of the balance, the calorimeter closed. On now finally adjusting the equilibrium of the balance, we observe if the wire swings freely through the several orifices through which it passes. The weight placed on the right-hand pan affords W, the weight of the substance, if, as should be arranged, equilibrium be previously obtained between the carrier and the pan. It is necessary also to see that the lower orifice of the calorimeter is closed with the wooden stop, and that the entrance-way for the steam-pipe at the back is also stoppered.

After these preparations the calorimeter must be left a sufficient

time to ensure that the thermometer and substance are uniformly at one and the same temperature. This interval of course varies with the nature and mass of the substance. In accurate work sufficient interval must be left to leave no doubt on the matter, the room being one not subject to sudden variations of temperature. When the required interval has elapsed, the thermometer is read by a hand lens, or better through a telescope. The temperature is noted down. The burner is now lighted beneath the boiler, all hot gas and steam being arranged to pass directly out of the room, as already mentioned, and direct radiation carefully screened off from the calorimeter. When the water is boiling, a second reading of the thermometer is taken and noted down. The boiler is now suffered to pass steam through the coupling-tube for about ten minutes, to ensure that all is free from air and mist. During this time it is better that the tube be directed so that the steam escapes up a flue or out of the room. The interval is to be utilised in checking the equilibrium of the balance, noting down the position of the rider, and observing if the valve on the boiler is working freely and without vibration. At the expiration of the interval, a third reading of the thermometer is taken and rapidly noted. It is then carefully withdrawn from the calorimeter, laid aside, and its tubulure stoppered with a little cork kept for the purpose. Everything is now ready for admitting steam. The steam-pipe, with its nozzle held upwards, is laid out along the slanting board which supports it between the boiler and the calorimeter. The nozzle is then grasped in the right hand, the steam-jet being still directed upwards. With the left hand we turn the thumb-screw commanding the exit tubulure at the bottom of the calorimeter, opening it to the full. The stopper closing the entrance-way to the rear of the calorimeter is now to be withdrawn, and then bringing the left hand back to the rubber steam-tube, we pinch it sharply at a convenient point, some 20 cm. below the nozzle, which, while the escape of steam is thus for the moment prevented, is run into its position. The steam tube is instantly released, and we give our attention to connecting by a switch the platinum spiral with the storage-cells. This only takes a moment, but by this time the steam is already pouring out at the exit way. For thirty or forty seconds it should be permitted to flow out freely ; what little condenses on the surrounding objects dries off quickly, and does no harm. The air being thus completely cleared out, the outflow of steam is moderated by closing the smaller tubulure against the exit-way, and in from one to three or four minutes, according to the nature and quantity of the substance, the weighing may be effected.

It will be at once seen by the balance if the substance is completely heated or not. If it is, it will be found that the vibration of the

pointer continues symmetrical, gaining only imperceptibly, perhaps, one division to the right in about five minutes. This will represent about half a milligram. Observed now for another five minutes, a similar addition will be needed. This increment is due to radiation, and the milligram thus accruing during the ten minutes is not to be included in the value, w_1, which we now have obtained.

The experiment is now concluded. It is well, after disconnecting it from the boiler, and while the calorimeter is still hot, to dry it out, as the residual heat then completes the drying very thoroughly. The corrections on w_1, necessary to convert it to the value w of the final equation have already been considered.

The Differential Steam Calorimeter.

In the use of the apparatus just described, it is certain that a high degree of accuracy is attained. In the thermometry and in the estimation of the weight of steam condensed upon the substance, an accuracy of one part in one thousand may, I think, generally be attained. There remain certain causes of error unknown in value within limits, as in all calorimetric methods. In other methods the substance is transferred from a region at one temperature to a region at another. The error of transference has in these cases to be considered. The movement of the substance, when at its highest temperatures, through the air, may be a source of serious error ; nor can this error be indefinitely diminished, for a too close approximation of the heater and the cooler causes a transference of heat between the two, in itself a source of error. In the method of mixtures a further source of error is to be found in the continued radiation of the calorimeter and evaporation of the water contained in it.

In the method of condensation the substance is not moved, but the medium around it is changed. Is there any error comparable with the error of transference in other methods ? There doubtless is some error, but it is not to be expected that it is at all as great. The error in this case is simply the radiation of the approaching vapour to the substance. Now the velocity with which the steam can be brought to fill the calorimeter is very great, and the momentary radiation of the advancing steam upon the substance is in part compensated by the precipitation of the most active part of this radiating steam upon the substance.

Radiation between the substance and its precincts now begins at a certain rate, the value of which when the temperatures become steady can easily be estimated. The first error is a minus error, the second a plus error. There may be also some minus error of the second sort. The errors thus tend towards a balance. All experimental work indicates that the resultant error is very small. Experiments

in which the surface extent of the same substance is varied con-siderably more especially point to this conclusion. If these are to be taken as conclusive, the error must be most generally less than the proportion one in a thousand. The variations in successive experi-ments are of about this magnitude, but are not in any special direction, and so point to no source of error in particular. These experiments are on conductors. (See "Method of Condensation," p. 362.)

The change of medium around the substance from one of greater to one possessing less buoyancy affects the balance and has to be allowed for by calculation based on experiment. It is improbable that more than a very small error arises from this source. Special cases may, however, arise in which this may not be so; and it was chiefly to avoid error from this last source that, in dealing with the large spheres of thin metal, used in the determination of the specific heat of air at constant volume, I resorted to the use of the differential calorimeter.* This has the further advantage of eliminating the radiation error affecting observations in the simple calorimeter. Nor need the thermal expansion of the substance any longer be con-sidered. I describe the apparatus briefly here, as it seems in fact to eliminate to a great extent, if not entirely, what small risk of error obtains in the previously described apparatus. Its advantages, how-ever, are most conspicuous in the use for which it was designed, the only use to which, up to the present I have applied it—the calori-metry of gases. Its application to this branch of physics must ever be its most important use. Indeed in the conditions obtaining in the calorimetry of solids or liquids it is hardly called for. However, even in these latter cases, where it is advisable to enclose the substance from contact with the steam, the differential calorimeter would enable us to effect the experiment somewhat more accurately than would be possible with the use of the single calorimeter.

Plate 7 shows, in side sectional elevation, fig. 2, and front sectional elevation, fig. 1, to a scale of one-tenth, the differential calorimeter which I have at present in use in dealing with gases. The spheres, one of which is used to hold the gas, are shown hanging in the calorimeter. The drawing needs little explanation after what has been said about the single calorimeter. The principle is obvious. Apart from its special application to gases, it may be said that the calorimeter is so constructed that carriers depending from both arms of the balance are hung within it, side by side and only a few centimetres removed from one another, the balance used being a short-beam balance. The substance may be enclosed in a receptacle of thin platinum or copper, with a screwed, air-tight lid, and placed upon one carrier; a similar receptacle, also

* "On the Specific Heats of Gases at constant Volume" (Preliminary Note) 'Roy. Soc. Proc.,' vol. 45, p. 33.

closed air-tight, permanently, if desired, is placed in the other carrier, but containing air only. The receptacles have been previously calorimetrically compared, and adjusted to have the same thermal capacity as they have the same external volume. Such receptacles are most conveniently constructed for dealing either with liquids or solids in small fragments. In these cases narrow-necked vessels, such as may be closed air-tight without difficulty, may be used. The calorimetric adjustment may of course be effected by inserting a calculated weight of copper or other substance of known specific heat in the vessel deficient in calorific capacity, or the difference may be allowed to remain and the constant recorded.

The thermometer enters the calorimeter midway between the carriers; and, as the calorimeter is of good conducting metal enclosed in an outer shield of wood, a uniform temperature may be assumed to prevail after some considerable interval of quiet has elapsed. Now, whatever this temperature, or the temperature of the steam, the receptacles and carriers alone are without effect upon the balance. Nor will there be any increment perceived due to radiation.* If one receptacle, however, contain a substance the balance will indicate a precipitation due solely to this substance. It is to be supposed that any error of transference of media will affect each receptacle alike, subsequent radiation will also affect them alike, and, as their volumes are identical, the varying buoyancy of the media is without effect on the balance.

I have said the precipitation will be due solely to the substance. Evidently, however, in very accurate work this cannot quite be assumed. In fact the thermal capacity of the air expelled from the one receptacle on the introduction of the substance must be considered. The precipitation due to this weight of air, considered as possessing the specific heat of constant volume, must be added to w, the observed effect upon the balance. As the air in these receptacles cannot be considered as dry air, this specific heat may be taken as having approximately the value 0·176. The volume of the substance must then, as with the use of the single calorimeter, be estimated, and the weight of air occupying this volume at the prevailing pressure and temperature calculated. For the pressure 760 mm., and temperature 10° C., if the steam temperature be assumed as 100° C., the addition to w is 0·000037 gram per c.c. of volume occupied by the substance.

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* To secure this result, I have found—what might be expected—that a similar condition of surface is necessary. With platinum vessels there would probably be little difficulty in attaining this; but with copper vessels I have found it necessary to keep both surfaces very free from grease and oxidised all over. Washing in ammonium hydrate and heating over a spirit flame seems to bring the surfaces to the desired uniform and permanent condition.

This will afford an idea as to the desirability of making the correction in any particular case. It is evident, too, that this additive correction, 0·000037 gram per c.c., might without further calculation be assumed as the correction in many cases, except very great accuracy be sought.

The construction of the differential calorimeter, it will be seen from Pl. 7, differs from that of the single calorimeter, in being single walled, and having a removable box-like covering of wood, fitted on over all, through which the thermometer is inserted, and which is placed in position after the calorimeter is closed. It is left on throughout the experiment. The obvious use of this box is to favour equilibrium of temperature throughout the calorimeter. Steam is admitted centrally, led from the boiler through a thin brass tube. The diameter conferred upon this tube in the calorimeter figured in the plate might with no disadvantage be reduced somewhat from that shown. This steam tube is in three lengths: an elbow piece fitting into the boiler; a straight horizontal piece of any required length; and finally a vertical double-tee piece. This last is capable of a rocking movement about the axis of its lower horizontal member, so that the upper horizontal member may be shifted either to a central position behind the calorimeter, when it is in the position for throwing steam into the calorimeter, or to one side, when it no longer communicates with the interior of the calorimeter. As drawn, it connects boiler and calorimeter. It is further necessary to provide the means of filling the whole steam pipe before filling the calorimeter. For this purpose the upper horizontal member of the double-tee tube is furnished with two swinging valves, closing it at each end. Before an experiment, and when the tee tube is turned to one side, the outer one of these is drawn inside for a couple of minutes till the whole steam way has been thoroughly cleared of air and heated throughout. During this time the rear orifice of the calorimeter is closed by means of a stopper of cork, bound in soft cloth. When the steam pipe is heated as described this is withdrawn, and the pipe simply shoved across till it comes to a stop provided. In this movement an automatic action lifts the inner valve, shoving it completely to one side, so that there is free way into the calorimeter. This, as will be readily understood, is effected by arranging that the edge of the hanging valve strikes against the projecting tubulure of the short steam way leading into the calorimeter. Subsequently, on inclining the tee piece to one side, the valve resumes its old position, closing the steam pipe. By this arrangement there is little or no leakage of steam, and the operation of turning steam into the calorimeter is effected by one movement of the hand.

There is but one exit way to the calorimeter. This is placed centrally at the bottom. Before experiment this is closed by means
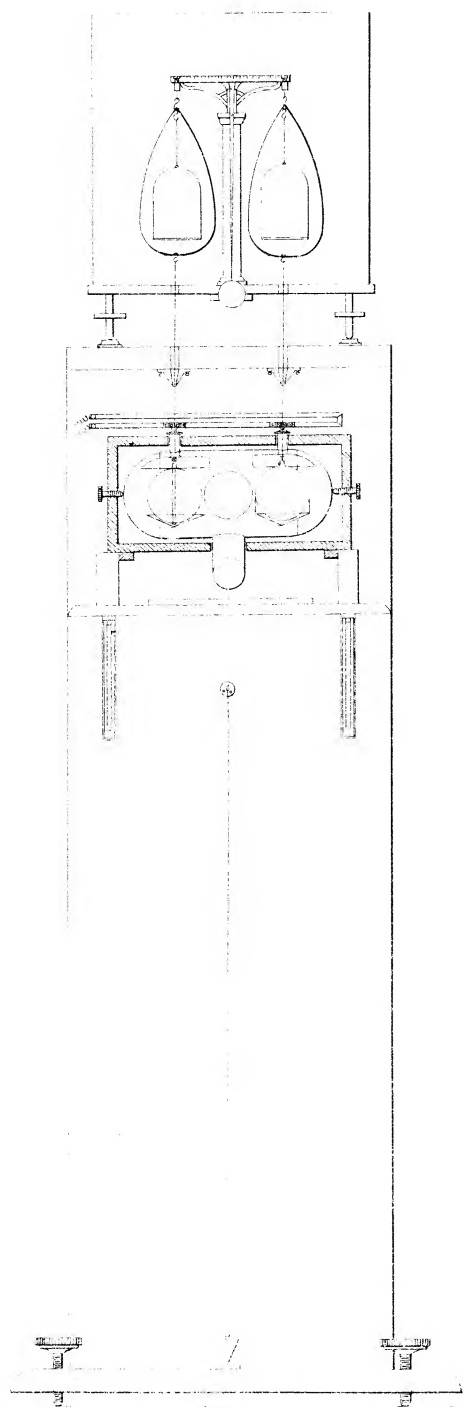
Fig. 1. Scale, One fourth.
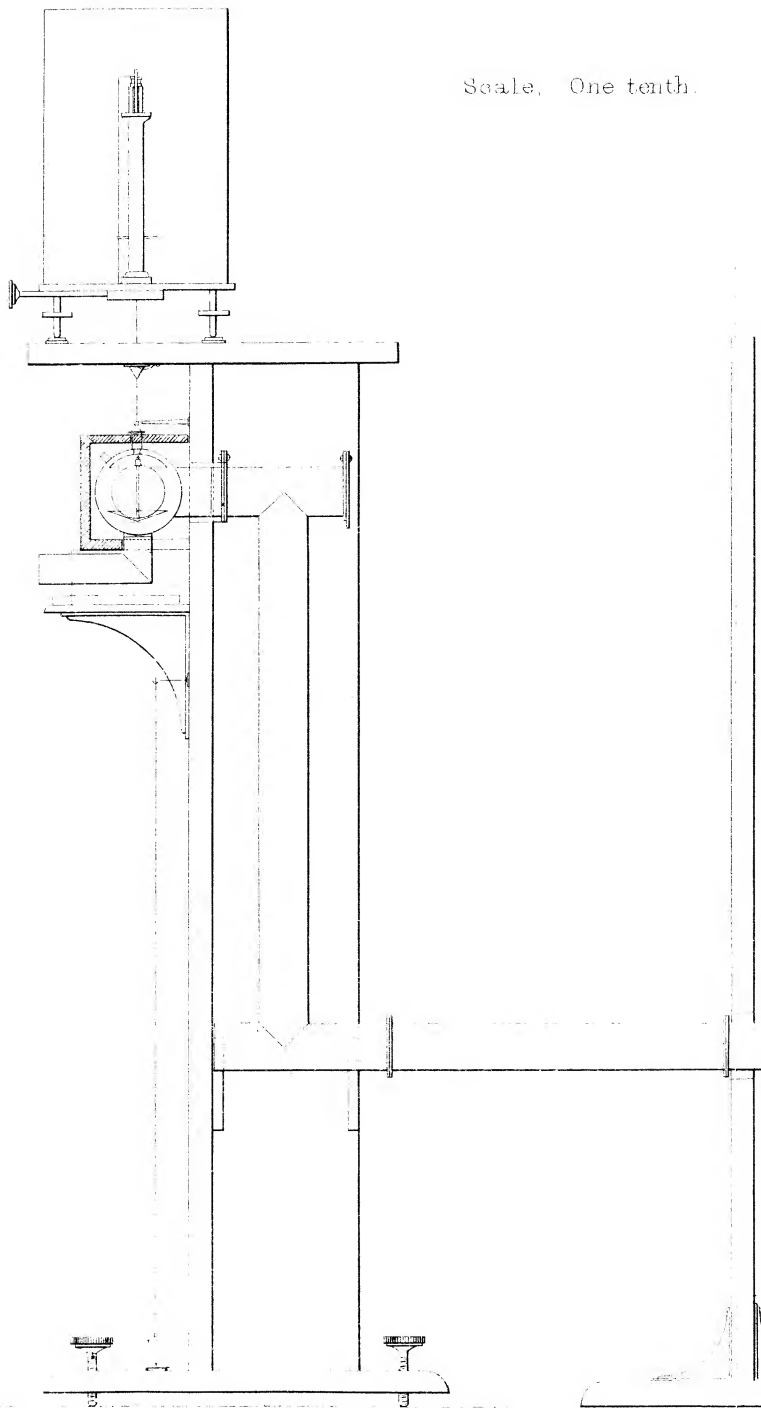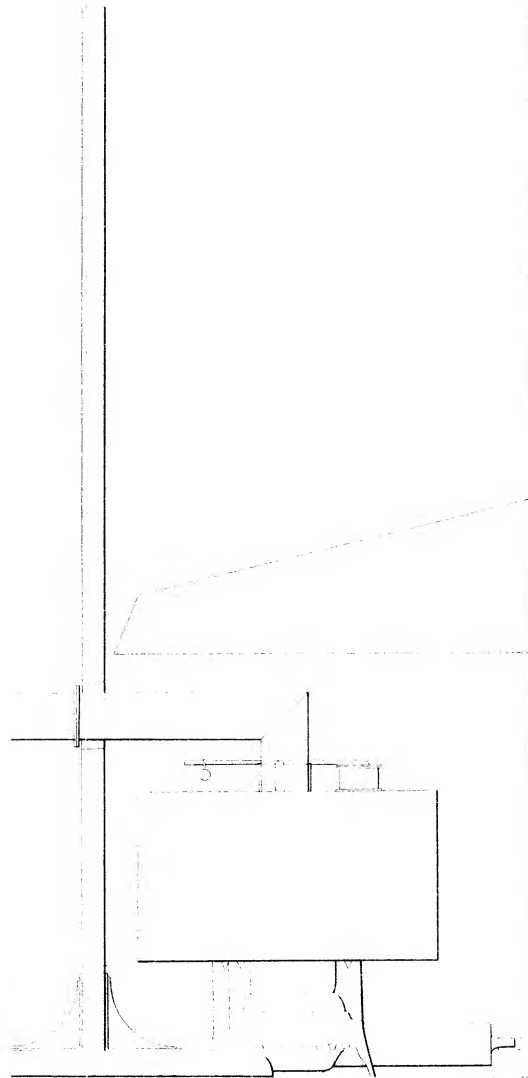
Fig. 2. Full size.
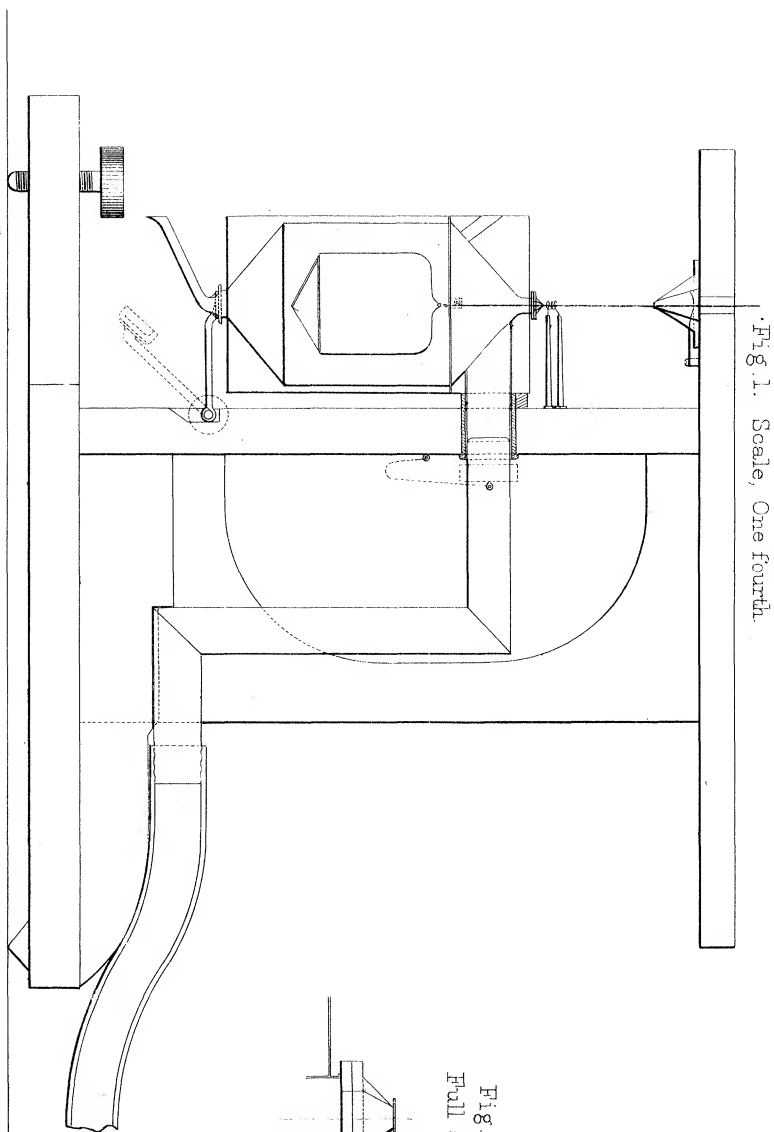
Scale, One tenth.

Fig. 1.

Fig. 2.

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of a cork ; this is removed when steam is first admitted. When the calorimeter is thoroughly filled it is replaced by a second cork, pierced by a short brass tube having a bore of about 7 mm. The diameter of this exit tube might also, with advantage, be reduced from that shown.

The platinum spirals used in drying and warming the suspending wires at their points of exit are in series, of the same length and fineness. The automatic adjustment at the orifices is applied, and, indeed, alone renders the differential arrangement workable. There is no difficulty in effecting the most accurate observation of weight.

The body of the calorimeter is cylindrical in form—a form used for its stiffness and inexpensiveness. The ends of the cylinder are closed by hemispherical caps of thin, spun copper. These have a swelled flange fitting smoothly over the ends of the cylinder, and are further kept in their places by two thumbscrews, fixed in the box covering the calorimeter, one at each end, and so located that when the box is in position and the screws screwed in, they will bear against the hemispheres. Owing to the shape of the calorimeter, it is necessary to shelter the carriers from drip by guards or umbrellas of thin Dutch metal, sprung on two projecting wires into the tubulures of the orifices, so that they can be removed and dried.

To allow of weights being placed on either side of the balance, the ordinary stirrups must be removed. The arrangement shown on the figure works well. Weights may be laid on or taken off the little inner pans without swinging the suspending wires supporting the carriers.

In conclusion, it may be worth remarking that many laboratory-instruction, or even lecture-table experiments of interest may be readily shown with the differential calorimeter. Thus the law of atomic heats is illustrated by placing quantities of two simple bodies, proportional to their atomic weights, in the calorimeter, and equilibrating by weights placed in the upper pans. On admitting steam, the equilibrium of the balance will (theoretically) remain undisturbed. Similarly Wœstyn's law of the constancy of specific heats of bodies in the free and combined states might be illustrated by placing the free elements in the proportions of chemical composition on one carrier, and an equal weight of the combined elements on the other.

The application of the vapour calorimeter to the determination of latent heats of vaporisation is very probably possible. I regret that neither this application of it, nor the allied question of the employment of other vapours besides that of water, can be considered here, the study of the capabilities of the steam calorimeter and a couple of its applications having occupied my time up to the present.
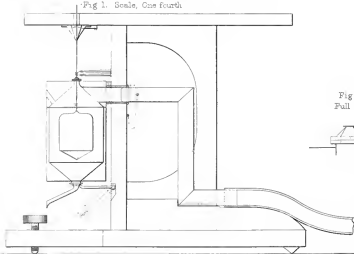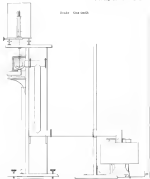
Fig 1. Scale, One fourth

Fig 2
Full size

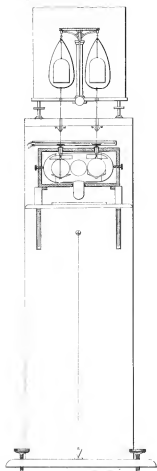Scale full width

Fig. 1.   Fig. 2.

Scale, One tenth

Fig.1

Fig.2

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